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# Nitramino- and dinitromethyl-substituted 1,2,4-triazole derivatives as high-performance energetic materials

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Dedication ((optional))

**Abstract:** Since highly nitrated single nitrogen rich heterocycles are important motifs in high energy density materials, extensive studies for the development of such novel molecules have been underway. A highly energetic moiety, 3-dinitromethyl-5-nitramino-1,2,4-triazole, which consists of a triazole ring, and nitramino and dinitromethyl groups, has been designed and synthesized. By pairing with nitrogen rich cations, several ionic derivatives were obtained. Theoretical and experimental studies show that the hydroxylammonium salt (7) is highly dense, and has excellent detonation performance with acceptable thermal stablity and sensitivities, which are superior to those of RDX.

#### Introduction

The development of high energy density materials (HEDMs) continues to give rise to the exploration for new materials with a detonation performance comparable to octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and an insensitivity of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB).<sup>[1]</sup> Being environmentally friendly is a concern that also needs to be considered. Many of the current synthesis strategies for energetic materials have focused on incorporating energetic groups into nitrogen rich heterocycles.<sup>[2]</sup>

Triazole rings have emerged as a class of promising synthetic building blocks that can be converted into a diverse range of energetic compounds due to their high positive heats of formation, ring strain and generation of environmentally friendly dinitrogen upon decomposition with a concomitant high order of energy release.<sup>[3]</sup> Many studies have been conducted on the combination of energetic groups with triazole or bis-triazoles.<sup>[4]</sup> With respect to insight into structure-property relationships, highly nitrated small-ring/single heterocycles are promising energetic materials arising from the additional energy release upon opening of the strained ring systems during decomposition.<sup>[5]</sup> Typical examples including 3,5bis(dinitromethyl)-1,2,4-triazole monoanion and dianion,<sup>[6]</sup> 5-(dinitromethyl)-3-(trinitromethyl)-1,2,4-triazole and its

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derivatives,<sup>[7]</sup> 5-nitro-3-trinitromethyl-1*H*-1,2,4-triazole,<sup>[5]</sup> and 3,5-dintramino-1,2,4-triazole<sup>[8]</sup> shown in Figure 1.





In our continuing mission of seeking energetic compounds by incorporating different energetic fragments into a single heterocyclic ring, a series of energetic salts based on a triazole ring-containing a nitramino group and a dinitromethyl group were designed and synthesized. All of the new compounds were fully characterized. In addition, the potential application of the new ionic compounds as energetic materials was experimentally and theoretically studied.

#### **Results and Discussion**

Attempts to introduce the nitro group into ethyl 2-(5-amino-1*H*-1,2,4-triazol-3-yl)acetate (1) by various nitration reagents have been studied.<sup>[5]</sup> However, it was difficult to isolate the product from the reaction mixture. After continuing to investigate this reaction, we found that ethyl 2-[5-(nitramino)-1*H*-1,2,4-triazol-3-yl]acetate (5) could be isolated from the nitration reaction of 1 by using a mixture of 100% nitric acid and concentrated sulfuric acid when the reaction time was 6 h. When the reaction time was extended to 24 h and after decarboxylation with methanolic ammonia, the ammonium salt **6** was isolated and characterized. However, the yield of each step was rather poor (Scheme 1).

After isolating and confirming the structure of **5**, a new synthetic route was designed as shown. The reaction started with diethyl malonate, which was treated with hydrazine monohydrate in ethanol to give ethyl 3-hydrazinyl-3-oxopropanoate (**3**).<sup>[9]</sup> Reaction of **3** with N-methyl-N-nitroso-N'-nitroguanidine generated ethyl 3-[2-amino(nitroimino)methyl]-hydrazinyl-3-oxopropanoate (**4**), which was treated with aqueous sodium hydroxide and was subsequently acidified to form **5**. The

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nitration of **5** with mixed acid gave the intermediate **2**, which was not isolated but treated with methanolic ammonia/hydroxylamine to give the corresponding energetic salts (**6** and **7**). Energetic salts (**9** – **14**) were synthesized by metathesis reactions of hydrochloride salts with the silver salt (**8**), which was prepared by treating **6** with two equivalents of aqueous silver nitrate. All of the new compounds were characterized by <sup>1</sup>H, and <sup>13</sup>C NMR, and IR, elemental analysis and single crystal X-ray diffraction of **6** and **11**.

The <sup>15</sup>N NMR spectra for 6 and 14 are shown in Figure 2. The signals are assigned based on comparison with compounds reported in the literature<sup>[10]</sup> and additional theoretical calculations B3LYP/6-311+g(2d,p) with IEF-PCM continuum solvation models<sup>[11]</sup> of Gaussian 03 software as well as analysis of <sup>1</sup>H-<sup>15</sup>N heteronuclear multiple bond correlation (HMBC, Supporting Information). For 6, the signal for the ammonium cation was observed at the highest field of  $\delta$  = -360.7 ppm. The signals for nitrogen atoms in nitramino (N1) and dinitromethyl groups (N6) are located at -18.8 and -23.9 ppm, respectively. Only two signals (N4 and N5) were found for the triazole ring due to fast proton exchange. In the spectrum of 14, the nitrogen atoms (N12/N13/N14) in the amino groups are found at -324.9 ppm at high field. According to the <sup>1</sup>H-<sup>15</sup>N HMBC spectrum (Figure S19, SI), the nitrogen atoms (N10 and N11) were found at -188.6 and -260.9 ppm, respectively. The chemical shifts (N1, N6, N4 and N2) in the anion of 14 are comparable to those in 6, while both of signals (N3 and N5) in the triazole ring are seen at  $\delta$  = -189.8 (N3) and -188.1 (N5) ppm.

Suitable crystals of **6** and **11** for single crystal X-ray diffraction were obtained by slow evaporation of their aqueous solutions. Compound **6** crystallizes in the orthorhombic P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> space

group with a calculated density of 1.744 g cm<sup>-3</sup> at 150 K. The



**Figure 2.** <sup>15</sup>N NMR spectra of **6** and **14** recorded in  $d_6$ -DMSO. The *x* axis represents the chemical shift  $\delta$  in ppm.

crystal structure is shown in Figure 3a. The hydrogen atom is located on N6 on the triazole ring, indicating that the deprotonation occurs at C10 and N4. The bond lengths of the triazole ring are between the length of the corresponding single and double bonds (C–N: 1.47 Å, 1.22 Å; N–N: 1.48 Å, 1.20 Å) <sup>[12]</sup>, N9–C5 (1.3397(16) Å) and N7–C8 (1.3270(17) Å) have a more double bond character, while N6–C5 (1.3475(16) Å) has a more single bond character. The nitramino group and the triazole ring are essentially coplanar (torsion angle: <O2-N3-N4-C5 = -1.42(19)°), while the atoms in the dinitromethyl group form another plane. The angle between the two planes is 76.34 °. The crystal packing of the compound is dominated by several

hydrogen bonds between nitrogen atoms and oxygen atoms (Figure 3b), the details are found in the SI.



**Figure 3.** (a) Crystal structure of **6**; thermal ellipsoids are drawn at the 50% probability level. (b) Packing diagram of **6** viewed down the *a*-axis. Unit cell indicated and dashed lines represent hydrogen bonding.

The trihydrate of the diaminoguanidinium salt, **11**·3H<sub>2</sub>O, crystallizes in the triclinic P-1 space group, with two formula units per unit cell (Z = 2). Due to the presence of three water molecules in the unit cell, it has a low calculated density of 1.625 g cm<sup>-3</sup> at 150 K. The molecular structure is shown in Figure 4a. The parameters in the anion are in good agreement with those described previously for **6**. In Figure 4b, the solid-state structure is dominated by hydrogen-bonding interactions between the anions and the diaminoguanidinium cations as well as the water molecules.



Figure 4. (a) Crystal structure of 11; thermal ellipsoids are drawn at the 50% probability level. (b) Packing diagram of 11 viewed down the *b*-axis. Unit cell indicated and dashed lines represent hydrogen bonding.

The UV-vis absorption spectra of **6** and **14** were measured in water solution (pH = 7.02) and shown in Figure 5. The UV-vis spectrum of **6** shows two strong absorption bands in the region of 250–450 nm, with maximum absorptions at 288 nm and 358 nm, respectively. The molar extinction coefficients are  $1.38 \times 10^4$  and  $1.54 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>, respectively. Similarly, compound **14** also exhibits maximum absorption peaks in the same positions.





The physicochemical properties of energetic salts **6–7** and **9–14** including thermal stabilities, detonation properties, heats of formation, and impact and friction sensitivities were determined. The results are given in Table 1. Most of new materials decompose at < 200 °C varying in the range between 143 to 185 °C, while **14** has the highest decomposition temperature of 208 °C, which is comparable to RDX. The heats of formation were calculated by Gaussian 03 software.<sup>[13]</sup> Compound **11** has a negative value due to the presence of water molecules. Compounds **6** and **9** also exhibit negative heats of formation, while the others have positive values arising from the increased nitrogen content. The heat of formation of **14** is 1131 kJ mol<sup>-1</sup> (2.09 kJ g<sup>-1</sup>), which is the most positive value found for these compounds

Densities were measured by a gas pycnometer at 25 °C. The hydroxylammonium salt **7** has a density of 1.805 g cm<sup>-3</sup>, while the others show moderate densities varying from 1.610 to 1.752 g cm<sup>-3</sup>. By using the measured densities and calculated heats of formation, the detonation velocities and detonation pressures were predicted based on traditional Chapman–Jouguet thermodynamic detonation theory using EXPLO5 6.01.<sup>[14]</sup> The calculated detonation pressures (*P*) for the new salts fall in the range of 22.6 (**9**) to 36.1 GPa (**7**), and the detonation velocities (*Dv*) are distributed between 7912 (**9**) to 9026 m s<sup>-1</sup> (**7**). The hydroxylammonium salt **7** exhibits an excellent detonation performance exceeding that of RDX.

Since these compounds have several nitro groups, which have potential application as energetic compounds, their impact and friction sensitivities were determined according to BAM standard technology.<sup>[15]</sup> The values of the impact sensitivities of these energetic compounds are between 10 J and 25 J. Although the hydroxylammonium salt (7) has a friction sensitivity of 240 N, the other compounds are more insensitive to friction (*FS*: 360 N).

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Comp	$ ho^{[a]}$	Dv <sup>[b]</sup>	<b>P</b> <sup>[c]</sup>	$\Delta H_{\rm f}^{\rm [d]}$	T <sub>dec</sub> <sup>[e]</sup>	IS <sup>[f]</sup>	FS <sup>[g]</sup>
Comp	(g·cm⁻³)	(m s <sup>-1</sup> )	(GPa)	(kJ mol <sup>-1</sup> /kJ g <sup>-1</sup> )	(° C)	(J)	(N)
6	1.710	8477	28.1	-91.3/-0.34	143	15	360
7	1.805	9026	36.1	25.0/0.08	168	10	240
9	1.649	7912	22.6	-50.4/-0.14	185	20	360
10	1.706	8447	26.3	171.1/0.45	159	18	360
11	1.610	8239	24.3	-50.7/-0.11	145	15	360
12	1.721	8906	29.7	638.9/1.40	165	18	360
13	1.734	8459	27.4	628.7/1.46	162	20	360
14	1.752	8615	28.3	1131/2.09	208	25	360
RDX	1.800	8795	34.9	70.3/0.32	204	7.5	120

Table 1. Energetic properties of the synthesized salts (6-7 and 9-14) compared to RDX.

[a] Density measured by a gas pycnometer at 25 °C; [b] Calculated detonation velocity; [c] Calculated detonation pressure; [d] Calculated molar enthalpy of formation in solid state; [e] Temperature of decomposition (onset); [f] Impact sensitivity; [g] Friction sensitivity.

#### Conclusions

In conclusion, in contrast to the direct nitration of 1 followed by decarboxylation which led to the formation of 6 at a low yield (12%), an improved synthetic route was designed. The ammonium salt (6) is readily prepared by nitration of 5, which was synthesized from diethyl malonate in a facile strategy. Several nitrogen rich energetic compounds based on 3dinitromethyl-5-nitramino-1,2,4-triazolate were obtained by decarboxylation or metathesis reactions. All of them were characterized and, in addition, 6 and 11 were studied by single crystal X-ray analysis. The energetic properties of these salts were examined. Among them, the hydroxylammonium salt (7) exhibits promising properties with a density of 1.805 g cm<sup>-3</sup>, a detonation velocity of 9026 m s<sup>-1</sup>, a detonation pressure of 36.1 GPa, and acceptable sensitivities (IS: 10 J; FS: 240 N), which suggest that it could be a promising candidate to replace the traditional RDX.

#### **Experimental Section**

**Caution:** The compounds described are potentially energetic materials that might explode under certain conditions, such as impact, friction or electric discharge. Although we have encountered no difficulties during their preparation and handling, they must be treated carefully. Since silver salt **8** is light sensitive, the process of making it and going through the next step should be kept in a dark environment. Appropriate safety precautions must be noted. Mechanical actions of these energetic materials, involving scratching or scraping, must be avoided. Manipulations must be carried out by using appropriate standard safety precautions.

#### General methods

All reagents were purchased from AKSci or Alfa Aesar in analytical grade and were used as received. <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) or 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer. Chemical shifts for <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectra are reported with respect to external (CH<sub>3</sub>)<sub>4</sub>Si (<sup>1</sup>H and <sup>13</sup>C) and CH<sub>3</sub>NO<sub>2</sub> (<sup>15</sup>N). [D<sub>6</sub>]DMSO was used as a locking solvent unless otherwise stated. Infrared (IR) spectra were recorded on an FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. The UV-vis spectra were measured with a Hewlett Packard 8453 UV-Visible Spectrophotometer. The pH was measured using a Vernier Labquest system. Density was determined at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Melting and decomposition (onset) points were recorded on a differential scanning calorimeter (DSC, TA Instruments Q2000) at a scan rate of 5 °C min-1. Elemental analyses (C, H, N) were performed on a CE-440 Elemental Analyzer or Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester.

#### **Computational Methods**

The gas phase enthalpies of formation were calculated based on isodesmic reactions (Scheme S1, SI). The enthalpy of reaction is obtained by combining the MP2/6–311++G<sup>\*\*</sup> energy difference for the reactions, the scaled zero point energies (ZPE), values of thermal correction (HT), and other thermal factors. For energetic salts, the solid-phase enthalpy of formation is obtained using a Born-Haber energy cycle.<sup>[16]</sup> For the compound which is a hydrate (**11**·2H<sub>2</sub>O), the solid-phase enthalpy of formation is obtained by adding the gas phase heat of formation of anhydrous compound to that of water (-241.8 kJ mol<sup>-1</sup>).<sup>[17]</sup>

#### X-Ray crystallography data

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A clear orange needle (6) of dimensions  $0.407 \times 0.364 \times 0.105 \text{ mm}^3$  was mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK<sub>a</sub> radiation ( $\lambda = 0.71073 \text{ Å}$ ). An Oxford Cobra low temperature device was used to keep the crystals at a constant 150(2) K during data collection.

A clear yellow chunk crystal (**11·3H**<sub>2</sub>**O**) of dimensions 0.249 × 0.175 × 0.062 mm<sup>3</sup> was mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a PHOTON 100 CMOS detector. The crystals were irradiated using a 1µs microfocus CuK<sub>a</sub> source ( $\lambda$  = 1.54178 Å) with Helios optics. An Oxford Cobra low temperature device was used to keep the crystals at a constant 150(2)K during data collection.

Data collection was performed and the unit cell was initially refined using *APEX3* [v2015.5-2].<sup>[18]</sup> Data reduction was performed using *SAINT* [v8.34A]<sup>[19]</sup> and *XPREP* [v2014/2]<sup>[20]</sup>. Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2014/2].<sup>[21]</sup> The structures were solved and refined with the aid of the program SHELXL-2014/7.<sup>[22]</sup> The full-matrix least-squares refinement on F<sup>2</sup> included atomic coordinates and anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were located from the difference electron-density maps and added using a riding model.

Ethyl 3-[2-amino(nitroimino)methyl]-hydrazinyl-3-oxopropanoate (4) N-methyl-N-nitroso-N'-nitroguanidine<sup>[23]</sup> (6.62 g, 45 mmol) was added in small portions to a suspension of  $1^{[5]}$  (5.84 g, 40 mmol) in water (50 mL) at room temperature. The reaction mixture was heated to 60 °C and stirred for 24 h. The resulting precipitate was collected by filtration, washed with cold water (80 mL), and dried in air to give 2 as a white powder (7.05 g, yield: 76%). <sup>1</sup>H NMR:  $\delta$  10.14 (s, 1H), 9.75 (s, 1H), 8.68 (s, 1H), 8.13 (s, 1H), 4.09 (q, 2H), 3.35 (s, 2H), 1.20 (t, 3H) ppm. <sup>13</sup>C NMR:  $\delta$  167.5, 165.7, 161.1, 60.9, 40.9, 14.1 ppm.

#### Ethyl 2-(5-(nitramino)-1*H*-1,2,4-triazol-3-yl)acetate (5)

Method A: Compound **1** (1.0 g, 5.9 mmol) was added to a mixture of 100% nitric acid (4 mL) and concentrated sulfuric acid (10 mL) at 0 °C. After stirring for 30 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and continue with stirring for 6 h. The reaction mixture was poured into 100 g ice-water, the precipitate was collected by filtration, washed with cold water (30 mL) and dried in air to give **5** (0.38 g, yield: 30%).

Method B: A solution of sodium hydroxide (0.8 g, 20 mmol) in water (10 mL) was added to a suspension of **4** (4.66 g, 20 mmol) in water (50 mL). The reaction mixture was heated at reflux for 2 h and cooled to room temperature and acidified with concentrated hydrochloric acid to pH ~ 1. The resulting precipitate was collected and washed with water and dried in air to give **5** (3.00 g, yield: 70%).

White solid.  $T_{d \text{ (onset)}}$ : 183 °C. <sup>1</sup>H NMR:  $\delta$  14.05 (br), 4.13 (q, 2H), 3.89 (s, 2H), 1.20 (t, 3H) ppm.  $^{13}$ C NMR:  $\delta$  167.5, 152.8, 145.1, 61.2, 31.7, 13.9 ppm. IR (KBr):  $\tilde{\nu}$  = 3294(m), 1723(s), 1616(s), 1572(s), 1508(m), 1446(w), 1403(w), 1382(w), 1322(m), 1259(w), 1224(m), 1089(w), 1022(w), 1011(w), 995(w), 875(w), 779(w), 721(w), 699(w) cm^{-1}. Elemental analysis for  $C_6H_9N_5O_4$  (215.17): Calcd C 33.49, H 4.22, N 32.55 %. Found: C 32.95, H 4.02, N 32.63 %.

Diammonium 3-dinitromethyl-5-nitramino-1,2,4-triazolate (6)

Method A: Compound 1 (1.0 g, 5.9 mmol) was added slowly to a cooled and well-stirred mixture of concerntrated sulfuric acid (10 mL) and 100% nitric acid (4 mL) at 0 °C. The temperature was allowed to warm slowly to room temperature over a period of 1 h, and the mixture was stirred for an additional 24 h. The solution was poured into ice water (100 g) and extracted with diethyl ether (20 mL × 3). The combined organic phases were dried over magnesium sulfate and filtered. The solvent was evaporated at ambient temperature under vacuum to give a light yellow oil to which ethanol (10 mL) was added. After 6 h, the yellow precipitate was collected by filtration, washed with ethanol (10 mL), and diethyl ether (10 mL) to give **6** (0.19 g, yield: 12%).

Method B: Compound 5 (1.0 g, 4.6 mmol) was added slowly to a cooled and well-stirred mixture of concentrated sulfuric acid (10 mL) and 100% nitric acid (4 mL) at 0 °C. The temperature was raised slowly to room temperature over a period of 1 h, and the mixture was stirred for an additional 24 h at this temperature. The solution was poured into ice water (100 g) and the solution was extracted with diethyl ether (20 mL × 3). The combined organic phases were dried over magnesium sulfate and filtered. The solvent was evaporated at ambient temperature under vacuum to give a light yellow oil to which was added ethanol (10 mL). The solution was stirred and methanolic ammonia (2 M, 4 mL) was added. After 6 h, the vellow precipitate was collected by filtration, washed with ethanol (10 mL) and diethyl ether (10 mL) to give 6 (0.70 g, yield: 52%). Yellow solid. T<sub>d (onset)</sub>: 143 °C. <sup>1</sup>H NMR: δ 7.18 (br) ppm. <sup>13</sup>C NMR: δ 156.9, 152.4, 127.9 ppm. IR (KBr):  $\tilde{v}$  = 3382(w), 1673(s), 1523(s), 1422(s), 1316(m), 1205(s), 1128(s), 1077(m), 983(m), 853(w), 824(vw), 784(w), 766(w), 753(w), 728(w), 662(w), 543(w) cm<sup>-1</sup>. Elemental analysis for C3H10N9O6 (268.17): Calcd C 13.44, H 3.76, N 47.01 %. Found: C 13.31, H 3.64, N 47.82 %. IS: 15 J. FS: 360 N.

# Dihydroxylammonium 3-dinitromethyl-5-nitramino-1,2,4-triazolate (7)

Compound 5 (1.0 g, 4.6 mmol) was added slowly to a well-stirred mixture of concentrated sulfuric acid (10 mL) and 100% nitric acid (4 mL) at 0 °C. The temperature was raised slowly to room temperature over a period of 1 h, and the mixture was stirred for an additional 24 h. The solution was poured into ice water (100 g) and extracted with diethyl ether (20 mL × 3). The combined organic phases were dried over magnesium sulfate and filtered, and the solvent was evaporated at ambient temperature under vacuum to give a light yellow oil to which was added ethanol (10 mL). Aqueous hydroxylamine (50% solution in water, 0.4 g) was added with stirring. After 6 h, a yellow precipitate was collected by filtration, washed with ethanol (10 mL) and diethyl ether (10 mL) to give 7 (0.63 g, yield: 45%). Yellow solid. T<sub>d (onset</sub>): 168 °C. <sup>1</sup>H NMR: δ 8.76 (br) ppm. <sup>13</sup>C NMR: δ 155.8, 150.3, 126.6 ppm. IR (KBr):  $\tilde{v}$  = 1684(w), 1518(s), 1470(m), 1399(m), 1239(s), 1135(w), 1090(w), 987(w), 828(vw), 746(w), 660(vw), 540(w) cm<sup>-1</sup>. Elemental analysis for  $C_3H_{10}N_9O_8$  (300.17): Calcd C 12.00, H 3.36, N 42.00 %. Found: C 12.04, H 3.03, N 40.75 %. /S: 10 J. FS: 240 N.

General procedure for preparing 9–14. The ammonium salt 6 (0.54 g, 2.0 mmol) was dissolved in water (30 mL); then silver nitrate (0.75 g, 4.4 mmol) was added. The reaction mixture was stirred for 2 h at room temperature. Silver salt 8 was obtained by filtration and washed with water (30 mL). Then 8 was suspended in water (40 mL), and two equivalents of a corresponding hydrochloride salt was added. The temperature of the reaction mixture was increased to 60 °C and it was science for 4 h. After removing the insoluble solids, the filtrate was concentrated to give the final products (9–14).

 $\begin{array}{l} \textbf{Diguanidinium 3-dinitromethyl-5-nitramino-1,2,4-triazolate (9) Yellow}\\ solid. $$T_{d\ (onset)}$: 185 °C. $^1H\ NMR: $$\delta$ 12.93 (br), 7.03 (6H) ppm. $^{13}C\ NMR: $$\delta$ 158.0, 156.4, 152.7, 127.8 ppm. IR (KBr): $$\vec{v}$ = 3450(w), 3174(w), 1665(s), $$1581(vw), 1544(m), 1515(w), 1459(m), 1403(w), 1388(w), 1341(m), $$1262(m), 1211(w), 1147(w), 1060(vw), 1045(w), 983(w), 737(w), 619(vw) $$cm^{-1}$. Elemental analysis for $C_8H_{13}N_{13}O_6$ (351.24): Calcd C 17.10, H 3.73, $$N$ 51.84 %. Found: C 17.25, H 3.59, $N$ 51.71 %. $$IS: 20 J. FS: 360 $$N$. } \end{array}$ 

**Di(diaminoguanidinium)** 3-dinitromethyl-5-nitramino-1,2,4-triazolate dihydrate (11) Yellow solid.  $T_{d \text{ (onset)}}$ : 145 °C. <sup>1</sup>H NMR:  $\delta$  8.83 (2H), 7.27 (2H), 4.64 (4H) ppm. <sup>13</sup>C NMR:  $\delta$  159.7, 156.5, 153.4, 127.6 ppm. IR (KBr):  $\tilde{v} = 3406(w)$ , 3265(w), 3141(vw), 1686(s), 1511(s), 1464(m), 1431(w), 1393(w), 1313w, 1221(m), 1172(w), 1119(m), 982(m), 860(vw), 819(w), 753(vw), 636(w), 596(w) cm<sup>-1</sup>. Elemental analysis for C<sub>5</sub>H<sub>22</sub>N<sub>17</sub>O<sub>8</sub> (448.34): Calcd C 13.39, H 4.95, N 53.11 %. Found: C 13.73, H 4.98, N 52.65 %. *IS*: 15 J. *FS*: 360 N.

**Di(triaminoguanidinium)** 3-dinitromethyl-5-nitramino-1,2,4-triazolate (12) Yellow solid. *T*<sub>d (onset)</sub>: 165 °C. <sup>1</sup>H NMR: δ 8.58 (3H), 4.49 (6H) ppm. <sup>13</sup>C NMR: δ 159.0, 157.0, 153.0, 128.2 ppm. IR (KBr):  $\tilde{v} = 3231(w)$ , 1587(s), 1508(m), 1494(m), 1421(m), 1364(w), 1288(w), 1242(m), 1150(m), 1097(w), 1023(w), 978(w), 947(w), 826(w), 787(w), 760(w), 749(w), 725(vw) cm<sup>-1</sup>. Elemental analysis for C<sub>5</sub>H<sub>20</sub>N<sub>19</sub>O<sub>6</sub> (442.34): Calcd C 13.58, H 4.56, N 60.16 %. Found: C 13.48, H 4.26, N 60.66 %. *IS*: 18 J. *FS*: 360 N.

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**Keywords:** Triazole • nitramino group • dinitromethyl group • energetic materials • nitration

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# FULL PAPER

Several energetic salts based on a highly nitrated triazole ring, 3dinitromethyl-5-nitramino-1,2,4triazole, were prepared. The hydroxylammonium salt shows promising energetic properties. Y. Tang, S. Dharavath, G. H. Imler, D. A. Parrish, J. M. Shreeve\*

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Nitramino- and dinitromethylsubstituted 1,2,4-triazole derivatives as high- performance energetic materials

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